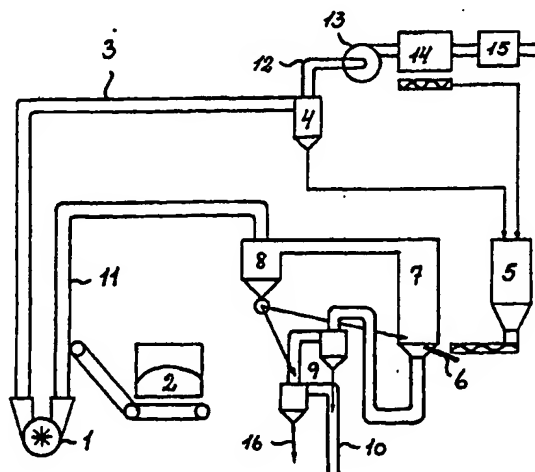




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>D21H 17/01, D21C 5/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/18885</b> <b>(43) International Publication Date:</b> 13 July 1995 (13.07.95)
<b>(21) International Application Number:</b> PCT/DK95/00001 <b>(22) International Filing Date:</b> 2 January 1995 (02.01.95) <b>(30) Priority Data:</b> 0012/94                      3 January 1994 (03.01.94)                      DK <b>(71) Applicant (for all designated States except US):</b> F.L. SMIDTH & CO. A/S [DK/DK]; Vigerslev Allé 77, DK-2500 Valby (DK). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ANDERSEN, Charlotte, Beicker [DK/DK]; Vigerslev Allé 77, DK-2500 Valby (DK). HUNDEBØL, Søren [DK/DK]; Vigerslev Allé 77, DK-2500 Valby (DK).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, DK (Utility model), EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** METHOD FOR MANUFACTURING OF A FILLER MATERIAL



**(57) Abstract**

The present invention relates to a method for manufacturing a filler from a mineral containing sludge which is a by-product from the manufacture of recycled paper. By the method according to the invention the sludge is introduced into a stream of hot gases from a burning chamber (7) and conveyed together with the gas stream to a drying and comminuting device (1) wherefrom the dry and finely divided paper material, suspended in the exit gas, is directed to a separator (4) in which the paper material is separated from the exit gas. The paper material is subsequently fired into the burning chamber and the organic content of the material is incinerated subject to development of heat. The mineral residue of the paper material which normally contains  $\text{CaCO}_3$ , kaolin and several minor components is calcined in the burning chamber for a suitable period of time at a controlled temperature, and finally the heat-treated material is cooled by means of air.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Method for manufacturing of a filler material.

The present invention relates to a method for manufacturing of a filler material from a sludge containing organic material material and calcium carbonate and/or kaolin.

5

By the term "filler" is meant a finely divided solid to be added to a liquid, semisolid, or solid composition, e.g. paint, paper, plastics or elastomers, to modify the properties of the composition, its colour and reduce its

10 costs.

In a filler material for e.g. paper are included several mineral components and a component which is frequently used is PCC (Precipitated Calcium Carbonate). PCC is often used  
15 together with another filler, viz. kaolin ( $(\text{Al}_2\text{O}_3) (\text{SiO}_2)_2 (\text{H}_2\text{O})_2$ ). The kaolin lends gloss to the paper, whereas the PCC gives the paper its bright white colour, and makes it soft and susceptible to ink and printing ink. The use of PCC in paper ranges between 5 and 40 per cent by weight,  
20 depending on the quality which is desired.

In connection with the manufacture of recycled paper on the basis of reclaimed waste paper, paper sludge is produced as a by-product, its main ingredients being cellulose fibres,  
25 printing ink and colour, water and a mineral residue of paper fillers, which mainly consist of PCC and/or kaolin.

The emergence of the paper sludge restrains the utilization of waste paper in the manufacture of recycled paper, be-  
30 cause the paper sludge is considered to be a waste product which has to be removed.

Until now the removing of the paper sludge has primarily been taken care of by depositing of the wet or dried paper  
35 sludge but depositing is causing problems in the form of malodors and/or emission of gaseous compounds.

In the Japanese patent application No. 80-2905 (filed on January 14, 1980), another method is disclosed according to which the paper sludge is initially dehydrated by mechanical means, whereafter the resulting filter cake is dried  
5 and granulated, and, finally, the granulate is used as a fuel in a cement kiln. The suggested solution in the above-mentioned patent application has the disadvantage that the paper sludge, of which 50% is typically water while 25% is a burnable substance, has to be transported  
10 from one plant to another, maybe distant, plant, which is disadvantageous in terms of cost efficiency. A further disadvantage is that a valuable mineral constituent, viz. the kaolin, is lost.

15 It is the object of the present invention to provide a method for manufacturing of a filler by heat treatment of paper sludge in such a way that the mineral components which is part of the paper sludge can be reused. By the present invention an environmentally acceptable method is  
20 thus indicated for treatment and reuse of paper sludge where the paper fibres are used as fuel and where it is possible to avoid the problems as e.g. malodors and emission of gaseous compounds which can arise in connection with the known methods of reuse and disposing.

25 According to the present invention the paper sludge is transformed into a product which can replace the materials which are normally utilized as fillers e.g. in paper, in plastic or rubber or is used for coating materials for  
30 paper or as pigment for paper, plastics or rubber. Hereby a recirculation loop is closed: instead of consuming expensive raw materials such as e.g. GCC (Ground Calcium Carbonate), PCC and kaolin, paper sludge is the primary raw material for the fillers.

35 According to the invention this is achieved by a method of

the kind mentioned in the introduction, where the paper sludge is introduced into a stream of hot exit gas from a burning chamber and passed together with the exit gas to a drying and comminuting apparatus wherefrom the dry and  
5 finely divided paper material is directed, suspended in the exit gas, to a separator in which the paper material is separated from the exit gas. The paper material is subsequently fired into the burning chamber and the organic content of the material is incinerated subject to  
10 development of heat, and in the burning chamber the mineral residue is calcined for a suitable period of time at a controlled temperature, and finally the heat-treated material is cooled with air.

15 The obtained product can now in accordance with known techniques be subjected to slaking, filtration and subsequent carbonization, thereby generating a product which can contain precipitated  $\text{CaCO}_3$ , a larger or smaller amount of kaolin and smaller amounts of titanium dioxide,  
20 silicium dioxide and/or other mineral compounds in dependence of the ratio between the mineral compounds in the paper sludge contained in the source material.

A method for carrying out the invention will be explained  
25 in further details in the following with reference to the drawing, where

Fig.1 shows a first embodiment of a plant for carrying out the method according to the invention,  
30

Fig. 2 shows a second embodiment of such a plant, and

Fig. 3 shows a third embodiment.

35 The plant shown in Fig. 1 comprises a drying and comminuting apparatus in the form of a drier crusher 1 which,

through a duct 11, is supplied partly with hot exit gas from the calciner 7 and partly with paper sludge, preferably mechanically dehydrated paper sludge, from a store 2. The dried and finely divided paper material is conveyed, 5 suspended in the drying gas, via a duct 3 and by means of the fan 13 to a separation cyclone 4 in which the paper material is separated from the exit gas and directed to an intermediate vessel 5.

10 The paper material is extracted from the intermediate vessel 5, for example by means of a screw conveyor, and it is fired into the plant's burning chamber, the calciner 7 via a burner 6, possibly in conjunction with oil or gas or some other back-up fuel. Hot combustion air is supplied to 15 the calciner from the cyclone cooler 9, causing the organic content of the paper material to be incinerated subject to development of heat. The mineral residue normally consisting mainly of  $\text{CaCO}_3$  and kaolin will, depending on the chosen temperature, become more or less calcined, i.e. with 20 expulsion of  $\text{CO}_2$  from the lime and  $\text{H}_2\text{O}$  from the kaolin. The temperature in the calciner will depend of the mineral composition of the paper sludge, expulsion of  $\text{H}_2\text{O}$  from the kaolin begins at  $400^\circ\text{C}$  and expulsion of  $\text{CO}_2$  from the  $\text{CaCO}_3$  may typically vary between  $800$  and  $1000^\circ\text{C}$ , which is sufficient for eliminating any toxic and/or malodorous compounds 25 in the paper sludge.

By controlling the atmosphere in the calciner 7 in a way that makes it either reducing or oxidising it is possible 30 to remove certain unwanted components as e.g. coloured components from the product.

The heat-treated material is carried, suspended in the combustion gases, to the separation cyclone 8, in which it 35 is separated from the gas and directed to the cyclone cooler 9. In this cooler it is cooled in counterflow with

fresh air from the fresh-air intake 10, while the air is simultaneously heated, and the finished product is extracted at the bottom of the cyclone cooler 9 at the outlet 16.

5

It is unavoidable that the drying gas in this plant can contain at least measurable concentrations of malodorous gases. The majority of such gases which may have been developed during the drying process in the drier crusher is reabsorbed on the dried paper during the transport in the duct 3, and thus passes down through the intermediate vessel 5 down in the calciner for destruction. The residual, nonabsorbed fraction of gases entrained in the stream 12 exiting the separation cyclone 4 must be removed from the drying gas prior to its release into the atmosphere. This may be accomplished by means of suitable exit gas cleaning equipment 15, for example a filter which contains cartridges of activated carbon or another suitable absorbent. Before the exit gas is vented to any such filter, it must, however, be cleaned of dust in a dust collector 14, and cooling of the exit gas, for example by air entrainment, may be required. The dust from the filter 14 may be supplied to the intermediate vessel 5, wherefrom it will be passed on to the calciner. It is a foregone conclusion that the cartridges in the filter 15, when at the end of their useful life and no longer capable of further absorption, can be disposed of by a method where they are pulverized and introduced into the calciner. As exit gas cleaning equipment 15 it will also be possible to use a scrubber in which the exit gas is washed with a suitable fluid.

In a second variant, Figure 2, the objective is to avoid usage of the exit gas cleaning equipment 15 for the drying gas, while still permitting the exit gas from the plant to be vented to the environment without any emissions of

organic compounds. The plant comprises, as is the case in Figure 1, a drying and comminuting device in the form of a drier crusher 1. Through the duct 11 the drier crusher 1 is fed with hot exit gas from the calciner 7 as well as paper sludge from the store 2. The plant incorporates a cyclone preheater 20, to which some of the exit gas from the separation cyclone 8 is supplied, whereas the rest of the exit gas is passed to the drier crusher 1. A pulverulent material, which is introduced at 21, is preheated in the cyclone preheater. This material may constitute a part of the plant product, which is recirculated from the outlet 16 of the cyclone cooler, or it may be ground limestone or kaolin, in case it is desirable to produce more filler than can be obtained from the paper sludge. The preheated powder is fed to the calciner via the duct 22, whereafter it is mixed in the calciner with the dried paper material from the vessel 5 and it is subjected to the same heat treatment as the mineral-containing residue of the paper material. The exit gas from the separation cyclone 4 of the drier crusher, which may contain organic compounds, is now passed, subsequent to dedusting in a filter 14, to the cyclone cooler 9. Here it is mixed with the preheated air which is sucked into the cyclone cooler through the fresh-air intake 10 and is heated in counterflow with the hot product from the separation cyclone of the calciner. The re-heated exit gas and air mixture are directed to the calciner, where the high temperatures ensure complete incineration of the organic compounds of the drying exit gas. It is seen that only pure exit gas can escape through the preheater 20 to the dust collector 23.

In a third variant, Figure 3, it is shown how the manufacture of filler may be combined with an existing lime kiln plant which incorporates a rotary kiln 30 with a preheater 31 to which the limestone is supplied at 32, and a dust collector 34. From the rotary kiln 30 an exit gas stream is



extracted to the drier crusher 1, and the dried and finely divided paper sludge is collected via a duct 3 and a separation cyclone 4 in the intermediate vessel 5. From here it is extracted and introduced through the main burner 33 of the rotary kiln into the burning zone 35 of the lime kiln. The mineral residue falls down on the limestone, and is carried by the movement of the rotary kiln under the flame together with the original raw material for calcination, and after cooling in a planetary cooler 37 the blended product 36 is extracted. The drying gas from the drier crusher 1 is conveyed by means of a fan 13 through the duct 3, the separation cyclone 4 and one more duct 12 to the planetary cooler 37 or more simply forward to the rotary kiln burner so that it can enter the burning zone for destruction.

The rotary kiln solution involves that the mineral residue is nodulized into balls, and, therefore, pulverization must be introduced in the subsequent treatment. In its simplest form, this may consist of dry slaking, and may involve that the dry product from the slaking machine is conveyed to a separator for classification into a fine and a coarse fraction, and that the coarse fraction is passed to a ball mill for grinding, and that it is subsequently returned to the separator as fine material. The fine material thus derived that mainly consists of lime hydrate and pulverized kaolin is now stirred in water, to which  $\text{CO}_2$  is added, and the precipitated product of PCC, kaolin and smaller amounts of other fillers is separated by filtration and constitutes the finished product which can be utilized as filler in paper, plastic or rubber manufacturing processes.

## PATENT CLAIMS

1. A method for manufacturing a filler from a sludge containing organic material and minerals, at least calcium carbonate and/or kaolin characterized in that the sludge is a paper sludge which is produced as a by-product during the manufacture of recycled paper.
2. A method according to claim 1, characterized in that the paper sludge is dried and finely divided and subsequently fired into a burning chamber where the mineral portion is calcined for a suitable period of time and at a controlled temperature and finally subjected to cooling.
3. A method according to claims 1 and 2, characterized in that the paper sludge is introduced into a stream of hot exit gas from the burning chamber (7,30) of the plant and in that it is passed together with the exit gas to the drying and comminuting apparatus (1) wherefrom the now dried and finely divided paper material is passed, suspended in the exit gas, to a separator (4) in which the paper material is separated from the exit gas, and in that the separated, dry paper material is fired into the burning chamber (7,30) in which the organic content of the material is incinerated subject to the development of heat, by means of which the mineral residue is heattreated for a suitable period of time and at a controlled temperature, and in that the heat-treated mineral is finally cooled in a cooler (9,37).
4. A method according to claim 3, characterized in that the exit gas which is separated in the separator (4) installed after the drying and comminuting device (1) is vented to a suitable exit gas cleaning apparatus (15).
5. A method according to claim 3, characterized in that the

exit gas which is separated in the separator (4) installed after the drying and comminuting apparatus (1) is returned while entrained in fresh air (10) to the burning chamber (7).

5

6. A method according to claim 3, characterized in that the burning chamber is a rotary kiln (30) and in that the exit gas which is separated in the separator (4) installed after the drying and comminuting device (1) is either directed  
10 through the cooler (37) or through the burner (33) back to the rotary kiln.

15

20

25

30

35

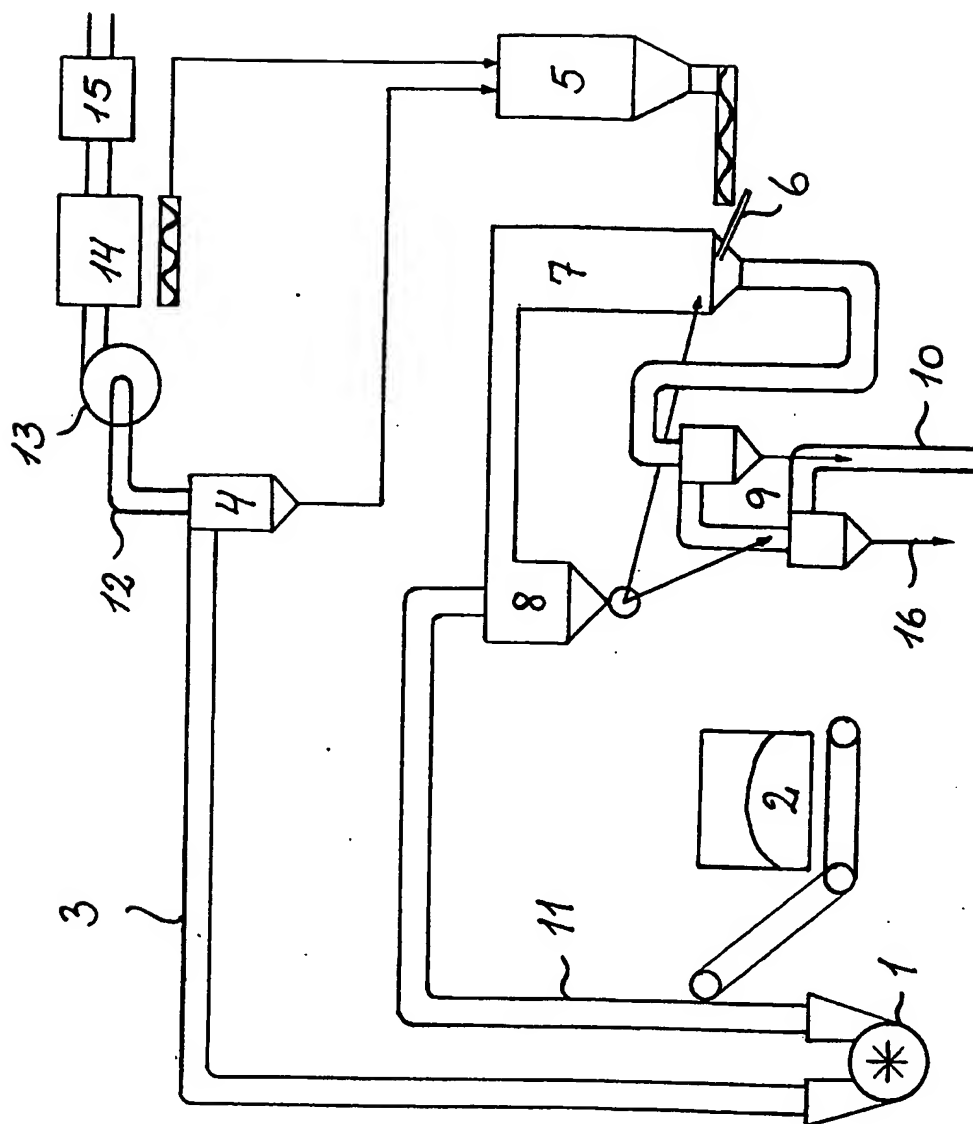
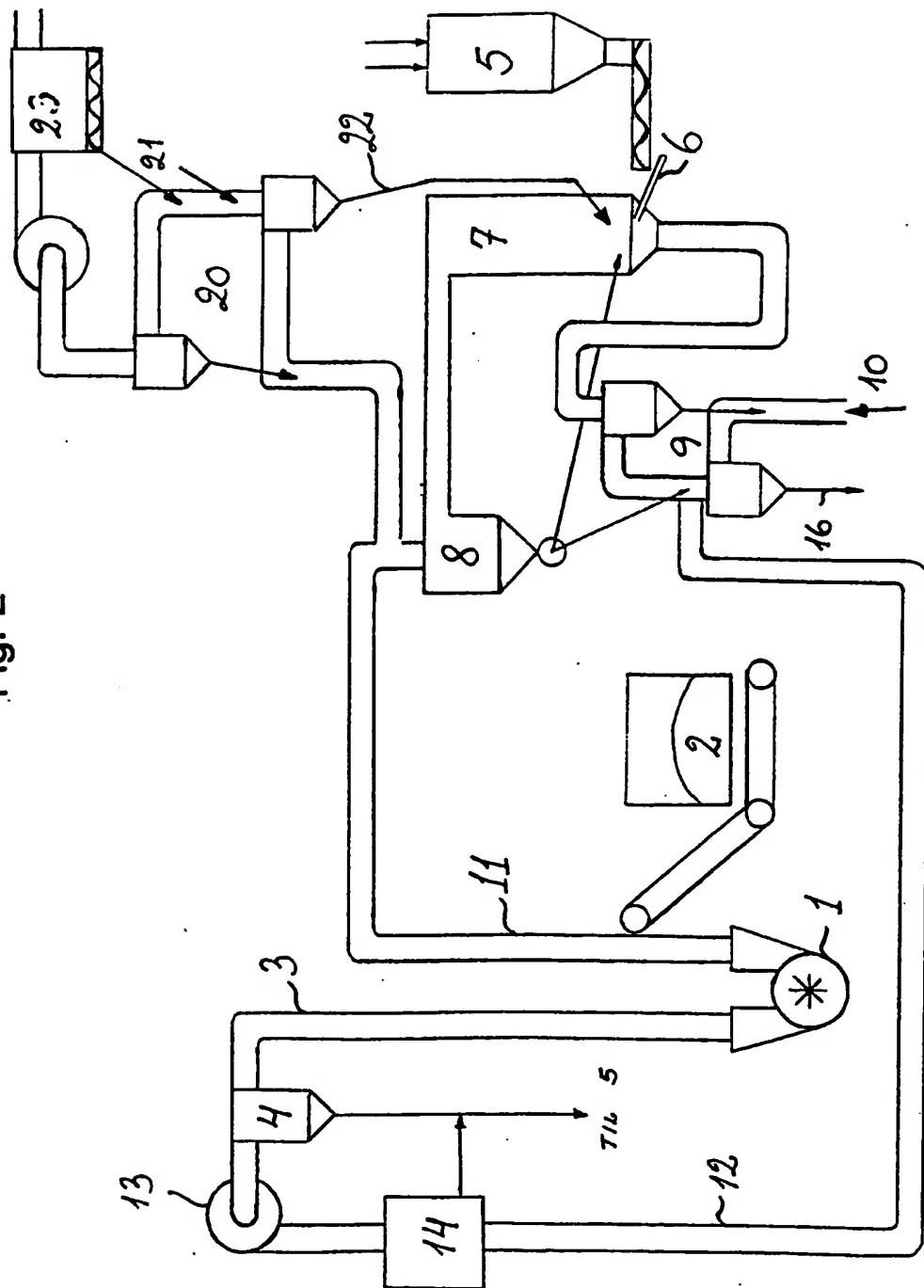


Fig. 1

Fig. 2



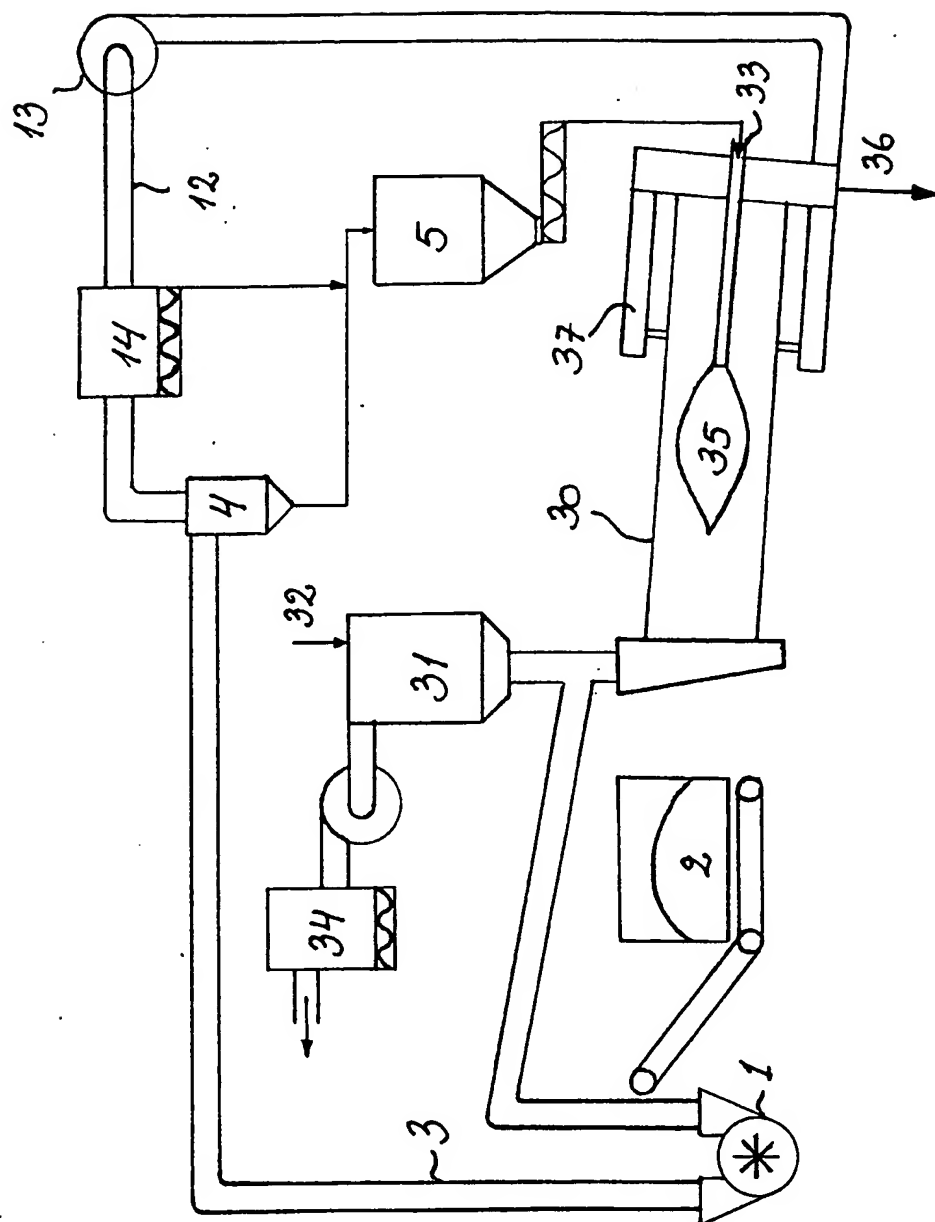


Fig. 3

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 95/00001

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC6: D21H 17/01, D21C 5/02 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC6: D21H, D21C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE,DK,FI,NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
WPI		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US, A, 5332474 (JOHN V. MAXHAM), 26 July 1994 (26.07.94), abstract --	1
X	US, A, 3876497 (CLARENCE A. HOFFMAN), 8 April 1975 (08.04.75), column 1, line 36 - column 2, line 65, claim 1 --	1-6
A	EP, A1, 0492121 (WOLTERS, PETER), 1 July 1992 (01.07.92) --	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
3 April 1995		18 -04- 1995
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer Barbro Nilsson Telephone No. +46 8 782 25 00

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 95/00001

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, A1, 9008220 (HENKEL KOMMANDITGESELLSCHAFT), 26 July 1990 (26.07.90)  -- -----	1



# INTERNATIONAL SEARCH REPORT

Information on patent family members

25/02/95

International application No.

PCT/DK 95/00001

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US-A-	5332474	26/07/94	NONE		
US-A-	3876497	08/04/75	CA-A-	976306	21/10/75
			DE-A,B,C	2256581	30/05/73
			GB-A-	1366020	04/09/74
			JP-C-	1085575	25/02/82
			JP-A-	48061709	29/08/73
			JP-B-	56027638	25/06/81
EP-A1-	0492121	01/07/92	CA-A-	2056889	21/06/92
			DE-C-	4108866	12/03/92
			JP-A-	4267953	24/09/92
WO-A1-	9008220	26/07/90	AU-B-	628922	24/09/92
			AU-A-	4949490	13/08/90
			CA-A-	2007735	14/07/90
			DE-A-	3900941	19/07/90
			EP-A,B-	0453489	30/10/91
			SE-T3-	0453489	
			ES-T-	2055413	16/08/94
			JP-T-	4502653	14/05/92
			US-A-	5232551	03/08/93